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FINAL REPORT

on the project

Molecular Orbital Studies in Oxidation: Sulfate Formation
and Metal-Metal Oxide Adhesion

NASA Grant No. NAG 3-341

Covering the period 10-30-82 through 7-31-85

by

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(NASA-CR-176070) MOLECULAR ORBITAL STUDIES
IN OXIDATION: SULFATE FORMATION AND
METAL-METAL OXIDE ADHESION Final Report, 30
Oct. 1982 - 31 Jul. 1985 (Case Western
Reserve Univ.) 5 p HC A02/NF A01 CSCL 11P G3/26

W85-32174

Unclas
21933

The purpose of this project was two-fold. The first was to determine the chemical mechanisms for sulfate formation from sodium chloride and sulfur trioxide, which is a product of jet fuel combustion. Molten sodium sulfate leads to "hot corrosion" of the protective oxide layers on turbine blades. The second goal was to determine how yttrium dopants in nickel-aluminum alloys used in turbine blades reduce the spalling rate of protective alumina films and enhance their adhesion. Both objectives were accomplished. In addition, two other sulfate mechanisms were deduced and structure of carbon monoxide on a clean chromium and clean platinum-titanium alloy surfaces was determined. All studies were by use of the atom superposition and electron delocalization molecular orbital (ASED-MO) theory. Seven studies were completed. Their titles and abstracts follow.

Mechanism for Forming Sodium Pyrosulfate from Sodium Chloride, Sulfur Dioxide, and Oxygen¹

Abstract: Energy and reaction pathway calculations show sodium pyrosulfate ($\text{Na}_2\text{S}_2\text{O}_7$) is more stable than sodium sulfate (Na_2SO_4) + $\text{SO}_3(\text{g})$. A common precursor to both products when formed on a NaCl surface is an $\text{SO}_2 + \text{O}_2$ adduct which transfers an oxygen atom to SO_3 . A low-energy barrier to this process is reached as the O_2 bond stretches and two electrons are transferred from chloride in the surface, yielding trigonal-pyramidal SO_4^{2-} which has two paths open to it. The lower-energy path has this SO_4^{2-} bond to SO_3 leading to pyrosulfate; the higher-energy path has this SO_4^{2-} take the tetrahedral sulfate structure. Cl_2 leaves the surface after the pyrosulfate or sulfate forms. Na^+ leaves the surface to bond to the anions. Both anions undergo low activation energy umbrella distortions, yielding tetrahedrally coordinated S. Our results offer strong theoretical support for the experimental results of Fielder, Stearns, and Kohl: specifically, (a) rate is proportional to SO_3 pressure; (b) $\text{Na}_2\text{S}_2\text{O}_7$ forms first at lower temperatures; (c) $\text{Na}_2\text{S}_2\text{O}_7$ decomposes, generating Na_2SO_4 ; and (d) Na_2SO_4 forms directly at higher temperature. At high temperatures the $T\Delta S$ contribution is larger than the ΔH contribution to ΔG , favoring sulfate formation even though it has a greater enthalpy than pyrosulfate at low temperatures.

Mechanism for Forming Hydrogen chloride and Sodium Sulfate from Sulfur Trioxide, Water, and Sodium Chloride²

Abstract: A molecular orbital study of sodium sulfate and hydrogen chloride formation from sulfur trioxide, water, and sodium chloride shows no activation barrier, in agreement with recent experimental work of Kohl, Fielder, and Stearns. Two overall steps are found for the process. First, gas-phase water reacts with sulfur trioxide along a pathway involving a linear $\text{O}\cdots\text{H}\cdots\text{O}$ transition state yielding closely associated hydroxyl and bisulfite which rearrange to become a hydrogen sulfate molecule. The hydrogen sulfate molecule transfers a hydrogen atom to a surface chloride in solid sodium chloride while an electron and a sodium cation simultaneously transfer to yield sodium bisulfate and gas-phase hydrogen chloride. This process repeats.

Both of these steps represent well-known reactions for which mechanisms have not been previously determined.

Adsorption of O_2 , SO_2 , and SO_3 on Nickel Oxide. Mechanism for Sulfate Formation³

Abstract: Calculations based on the atom superposition and electron delocalization molecular orbital (ASED-MO) technique suggest that O_2 will adsorb preferentially end-on at an angle 45 deg from normal on a nickel cation site on the (100) surface of NiO. SO_2 adsorption is also stronger on the nickel site; SO_2 bonds through the sulfur atom in a plane perpendicular to the surface. Adsorption energies for SO_3 on the nickel and oxygen sites are comparable in the preferred orientation in which the SO_3 plane is parallel to the surface. The calculations suggest that the strength of adsorption varies as $O_2 > SO_2 > SO_3$. On activation, SO_3 adsorbed to an O^{2-} site forms a trigonal pyramidal SO_4 species which yields, with a low barrier, a tetrahedral sulfate anion. Subsequently the anion reorients on the surface. Possibilities for alternative mechanism which require the formation of Ni^{3+} or O^{1-} are discussed. $NiSO_4$ thus formed leads to the corrosion of Ni at high temperatures in the SO_2+O_2/SO_3 atmospheres, as discussed in the experimental literature.

Mechanism for Chelated Sulfate Formation from SO_2 and Bis(Triphenylphosphine) Platinum⁴

Abstract: Structure and energy surface calculations using the atom superposition and electron delocalization molecular orbital theory show that the first step in the reaction between SO_2 and the dioxygen complex is the coordination of SO_2 with one oxygen atom of the complex, followed by metal-oxygen bond breaking and reorientation, leading to a five-membered cyclic structure. This then rearranges to form the bidentate coordinated sulfate. Alternative pathways are considered and are found to be less favorable.

Dopant Effect of Yttrium and the Growth and Adherence of Alumina on Nickel-Aluminum alloys⁵

Abstract: The atom superposition and electron delocalization molecular orbital theory and large cluster models have been employed to study cation vacancy diffusion in $\alpha-Al_2O_3$ and the bonding of $\alpha-Al_2O_3$ to nickel, aluminum, and yttrium surfaces. Al^{3+} diffusion barriers in $\alpha-Al_2O_3$ by the vacancy mechanism are in reasonable agreement with experiment. The barrier to Y^{3+} diffusion is predicted to be much higher. Since addition of yttrium to transition metal alloys is known to reduce the growth rate and stress convolutions in protective alumina scales, this result suggests the rate-limiting step in scale growth is cation vacancy diffusion. This may partially explain the beneficial effect of yttrium dopants on scale adhesion. The theory also predicts a very strong bonding between alumina and yttrium at the surface of

the alloy. This may also be important to the adhesion phenomenon. It is also found that aluminum and yttrium atoms bond very strongly to nickel because of charge transfer from their higher lying valence orbitals to the lower lying nickel s-d band.

**CO Adsorption on (111) and (100) Surfaces of the Pt₃Ti Alloy.
Evidence for Parallel Binding and Strong Activation of CO⁶**

Abstract: An ASED-MO study has been made of CO adsorption on a 40 atom cluster model of the (111) surface and a 36 atom cluster model of the (100) surface of the Pt₃Ti alloy. Parallel binding to high coordinate sites associated with Ti and low CO bond scission barriers are predicted for both surfaces. The binding of CO to Pt sites occurs in an upright orientation. These orientations are a consequence of the nature of the CO π donation interactions with the surface. On the Ti sites the π orbitals donate to the nearly empty Ti 3d band and the antibonding counterpart orbitals are empty. On the Pt sites, however, they are in the filled Pt 5d region of the alloy band, which causes CO to bond in a vertical orientation by 5σ donation from the carbon end.

Why CO Bonds Side-on at Low Coverage and Both Side-on and Upright at High Coverage on the Cr(110) Surface⁷

Abstract: An atom superposition and electron delocalization molecular orbital study of CO adsorption on the Cr(110) surface shows a high coordinate lying-down orientation is favored. This is a result of the large number of empty d-band energy levels in chromium, which allows the antibonding counterparts to σ and π donation bonds to the surface to be empty. When lying down, back-bonding to CO π^* orbitals is enhanced. Repulsive interactions cause additional CO to stand upright at $>\frac{1}{4}$ monolayer coverage. Our results confirm the recent experimental study of Shinn and Madey.

References

1. Mechanism for Forming Sodium Pyrosulfate from Sodium Chloride, Sulfur Dioxide, and Oxygen, A. B. Anderson and S. C. Hung, J. Am. Chem. Soc. 105, 7541 (1983).
2. Mechanism for Forming Hydrogen Chloride and Sodium Sulfate from Sulfur Trioxide, Water and Sodium Chloride, A. B. Anderson, J. Am. Chem. Soc. 106, 6262 (1984).
3. Adsorption of O₂, SO₂, and SO₃ on Nickel Oxide. Mechanism for Sulfate Formation, S. P. Mehandru and A. B. Anderson, to be published.
4. Mechanism of Chelated Sulfate Formation by Reacting SO₂ with Bis (triphenylphosphine) Platinum: A Theoretical Study, S. P. Mehandru and A. B. Anderson, Inorg. Chem. 24, 2570 (1985).
5. Dopant Effect of Yttrium and the Growth and Adherence of Alumina on Nickel-Aluminum Alloys, A. B. Anderson, S. P. Mehandru, and J. Smialek, J. Electrochem. Soc. 132, 1695 (1985).
6. CO Adsorption on (111) and (100) Surfaces of the Pt₃Ti Alloy. Evidence for Parallel Bonding and Strong Activation of CO, S. P. Mehandru, A. B. Anderson and P. N. Ross, to be published.
7. Why CO Bonds Side-on at Low Coverage and both Side-on and Upright at High Coverage on the Cr(110) Surface, S. P. Mehandru and A. B. Anderson, to be published.